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POLYMERIC MATERIAL AND

USE THEREOF

Commissioner for Patents

Alexandria, VA 22313-1450

DECLARATION

Sirs:

I, Hitoshi Kanazawa, declare that I am a citizen of Japan, of 27 Harada, Arai, Fukushima-shi, Fukushima Prefecture 960-2156

That I have studied at the Tokyo Institute of Technology, Research Course of Science and Engineering with a Doctor's degree of Polymer Science in 1976.

That I am a Professor of Department of Education, Fukushima University at Fukushima-shi 960-1296, Fukushima, Japan.

That I am the inventor and familiar with the above-identified application and have conducted the following experiment to demonstrate the difference between the present invention and the prior arts.

(1) In order to observe the effect of the method of J'752, its example (as Comparative Example 9) and an example based on the present invention (as Example 34) were carried out.

Comparative Example 9:

A polystyrene film (size 5 x 5 cm and thickness 0.2 mm) was exposed to a corona discharge for 90 seconds as an activation step. Then, an aqueous solution of PVA (10 weight %) was coated on the film and dried at 80 °C. When the polymer coated polystyrene film was washed in a boiling water, the coating layer was removed. In addition, the surface layer was peeled off in the cross cut test with an adhesion tape.

Example 34:

A polystyrene film similar to that used in the Comparative Example 9 was exposed to a corona discharge for 180 seconds as an activation step. Then, a trace of carbonyl groups on the film was observed by an IR spectroscopy. Then, the film was treated with an aqueous solution of PVA (10 weight %) containing 40 mg of potassium persulfate for one hour at 80 °C. The wettability of the product was markedly modified. The contact angle of water to the product was 25 degree while that of the untreated polystyrene film 120 degree. When the product was washed with a boiling water, the wettability was kept as it was.

These results support the aspect that the hydrophilic polymer is bound to the substrate by a strong chemical bond.

(2) In order to observe the effect of the method of J'884, following Comparative Example 10 was carried out.

Comparative Example 10:

According to the example of J'884, polyester fiber and polypropylene fiber were treated with a silicone resin by the padding-drying-curing method. The attached silicone resin to polyester fiber was completely removed after the three times of washing with boiling water and that of polypropylene fiber

was removed after a washing with boiling water.

(3) In order to demonstrate the advantageous effect of the present invention compared to the method of Grobe the following Example 35 was carried out.

Example 35:

A silicon rubber device or a PP film was treated by a plasma oxidation for 20 seconds. The treated polymer substrates were observed by an IR spectroscopy, however, the formation of carbonyl groups was not estimated. On the other hand, the formation of carbonyl groups was observed by the plasma treatment for 180 seconds according to the method of claimed in the Claim 28 of the present application. After this activation step, the polymer substrate was treated with hydrophilic polymer in the presence of a cerium (IV) salt according to Claim 28. Furthermore, the obtained product was carried out by a monomer grafting according to Claim 29. The obtained product gave an effective and durable properties in a hydrophilic property, water absorption property or adhesion property as compared with the products in Valint or Grobe III's methods.

(4) The following experiments were conducted in order to compare the effect of Ikada et al.'s method (as Comparative Example 11) and the method of the present invention (as Example 36).

Comparative Example 11:

According to Example 2 in Ikada et al.'s patent, a PP film was exposed to corona discharge for 80 seconds. After this treatment, the formation of carbonyl groups was observed by IR spectroscopy. However, the ratio of absorbance at around 1710cm⁻¹ to that at around 973 cm⁻¹ was not changed in before and after

the treatment. Then, a grafting of vinylpyrrolidone was carried out in the same manner as the Example 2. The weight increase of the obtained PP film was 1 weight % and the contact angle of water of the film was 30 degree. However, when the obtained PP film was washed in boiling water two times, the polyvinylpyrrolidone seemed to be removed completely because its contact angle of water became 120 degree (a value for untreated PP film). This result suggests that the formation of chemical bonds was not obtained.

Example 36:

- 1) PP film was exposed to corona discharge for 180 seconds and a trace of carbonyl groups was confirmed by IR spectroscopy.
- 2) Then, the treated PP film was put in a solution of PVA and potassium peroxide in methanol and water. The reaction mixture was kept at 80 degree C for two hours.
- 3) Then, the product of 2) was dipped in an aqueous solution of vinylpyrrolidone. As an initiator, a solution of azobisisobutyronitrile in methanol was added in the solution. A UV irradiation to the reaction mixture was carried out for 30 minutes.
- 4) The product obtained in 3) was washed with boiling water. The obtained PP film gave a value of contact angle of water less than 5 degree. Thus, a polyvinylpyrrolidone-grafted PP film was prepared. The obtained PP film gave a good adhesion property to paper with a starch glue.
- (5) The following experiments were conducted in order to compare the effect of the method of J'207 and the method of the present invention.

The example 1 in J'207 was followed; PE porous film was treated for 0.1 sec. by corona discharge under output of 7W/m² min at 35deg.C. After 50 seconds, the PE film was dipped in a solution of polypropyleneglycol in acetone (concentrtrion=30 weight %) for 5 minutes. The obtained PE film was washed with water and dried. The product gave a wettability to water. However, when the product was washed with an aqueous detergent solution at the boiling point for 5 minutes. The hydrophilic property of the PE film was decreased completely. The contact angle of water to the film became 120 degree from 30 degree. In addition, the hydrophilic layer of the product by J'207 was easily peeled by the cross cut test.

On the other hand, the similar treatment of a PE porous film was carried out according to the present claim 28. PE film was treated for 180 seconds by a corona discharge at 35deg.C. A trace of the formation of carbonyl groups was ascertained by IR spectroscopy. Then, the PE film was dipped in an aqueous PVA solution (concentration=10 weight %) for two hours at 70 degree C in the presence of KPS as a catalyst. The obtained PE film was washed with a boiling aqueous detergent solution for 5 minutes. The product gave a good hydrophilic property. It gives a contact angle of water to be 30 degree. Furthermore, in a cross-cut test with an adhesive tape, the hydrophilic property of the surface of the film was not revealed off.

Therefore, the method of J'207 is considered to give the polymer material simply coated with a hydrophilic polymer. However, the present invention gives real chemical linkage between activated polymer substrate and hydrophilic polymer.

(6) Young et al.'s method was examined as follows:

PP fibers (2d and 10 cm length) (0.5 g) was exposed to corona discharge for 30 seconds or ozone for 10 minutes. As no description about the extent of activation was described in Young et al.'s patent, the activation condition of the present invention was used.

The obtained fibers were treated with a binder, PRIMACOR 4990 which was used in their patent by spraying or dipping in the absence of any catalysts. The mixture of the fiber and the binder was heated, pressed, solidified and dried, and a board of the product was obtained. When the product was washed with boiling water for five minutes twice, the fibers were removed from the binder. Therefore, it is considered that the PP fiber and the binder did not make chemical bonds but an adhesion. The product cannot be used for the application which needs a durable hydrophilic property such as mentioned in Claims 46, 48-53, 55-57 and 59.

(7) The following experiments were conducted in order to compare the effect of the method of Wang et al. (as Comparative Example 12) and the method of the present invention (as Example 38).

Comparative Example 12:

A silicone resin board was used as a substrate instead of a silicone tube used in their Example 1. The substrate was dipped in a solution of benzoylperoxide in tetrahydrofuran for 30 second and dried. Then the substrate was put in a glass tube together with an aqueous solution of N,N-dimethylacrylamide, acrylamide, diacrylate, NaCl and polyvinylpyrrolidone. After sealing, the glass tube was kept at 87 degree C for 3 hours with a stirring.

The product was washed with boiling water five minute three times

(in the case of Wang et al., the washing was described to be made in water). After drying, a contact angle of water to the product was observed to be 120 degree. Thus, the wettability of the substrate was not modified by this method.

Example 38 :

The silicone resin board similar to that used in the above comparative example was used as a substrate. The method of the Claim 31 of the present invention was employed.

- 1) Solvent treatment: the substrate was dipped in toluene at 50 degree C for 30 minutes, and washed with methanol and dried.
- 2) Activation step: the substrate was exposed to ozone for 30 minutes. After the step, the formation of carbonyl groups was confirmed.
- 3) Hydrophilic polymer treatment: the substrate was dipped in an aqueous solution of polyethylene glycol containing potassium persulfate at 100 degree C for two hours.
- 4) monomer grafting; the product of 3) (substrate) was dipped in an aqueous acrylic acid solution containing cerium ammonium nitrate, and the mixture was exposed to UV irradiation for 30 minutes.

After these steps, a silicone board with a wettability to water and an improved adhesion property was obtained.

Thus, in the Wong's patent, there are not an activation step and a monomer grafting after a hydrophilic treatment which are important for the present invention.

(8) The following experiments were conducted in order to compare the effect of the method of Bamford et al. (as Comparative Example

13) and the method of the present invention (as Example 39).

Comparative Example 13:

Poly(hydroxyethyl acrylate) was subbed on a polypropylene film (size 5 x 5 cm) and dried. Then, a grafting of acrylic acid to the PP film was carried out using potassium persulfate for three hours at 80°C. The obtained substrate was washed with a boiling water for five minutes three times. The grafting % was not estimated. The obtained specimen did not give an apparent wettability to water.

Example 39:

A polypropylene film (size 5 x 5 cm) was treated with ozone for 20 minutes. A trace of the formation of carbonyl groups on the film was confirmed by IR spectroscopy. Then, the specimen was put in a solution of potassium persulfate (40mg) and poly(hydroxyethyl acrylate) (concentration 5 weight %) in water and methanol (its volume ratio, 9/1) and this reaction mixture was allowed to stand at 80°C for two hours. The obtained specimen was washed in a boiling water for five minutes three times. The obtained PP film gave a contact angle of water, 30°, while its untreated one 120°. The obtained PP film gave a good adhesion property with a PVA glue.

Therefore, their method is different from the present invention. As a result, the durable modified properties such as hydrophilic property, water adsorption property and adhesive property can not be obtained by the method as compared with the present invention.

The undersigned declarant declares further that all statements made herein of my own knowledge are true and that all statement made on information and belief are believed to

be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 10 day of February, 2004.

H. Kanazawa

Hitoshi Kanazawa